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Specification and Drawings, as originally filed, with Application for Patent Serial No: **2,418,546**, on February 6, 2003, by **INSTITUT NATIONAL DE LA RECHERCHE SCIENTIFIQUE**, assignee of Mario Bergeron and Marc Richer-Laflèche, for "A Method for Increasing the Chrome to Iron Ratio of Chromites Products".

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ABSTRACT OF THE DISCLOSURE

A method for increasing the chrome to iron ratio of chromite product selected from the group consisting of ore and ore concentrate comprising the steps of contacting a mixture of the chromite product, a salt such as NACl or any other adequate salt or combination of salts, chlorine and carbon monoxide in a reactor maintained at a temperature between about 250° and about 750° C whereby a portion of iron oxide in converted into gaseous iron chloride. In specific embodiments, the mwthod may comprise any of the following steps:the excess of chlorine gas leaving the reactor is contacted with scrap of iron metal in a washing tower and transformed in aqueous iron chloride, the condensed iron chloride is washed from the condenser and mixed with the iron chloride flux exiting the washing tower and reacted with NaOH to produce NaCl which is subsequently electrolyzed to NaOH and Cl_2 which are recycled in the process as reagents, the unreacted carbon monoxide is burned with air to yield carbon dioxide. The solid material produced, with a high chrome to iron ratio, is useful as a starting material for the production of enriched ferrochromium.

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TITLE OF THE INVENTION

A METHOD FOR INCREASING THE CHROME TO IRON RATIO OF CHROMITES PRODUCTS

FIELD OF THE INVENTION

The present invention relates to a method for increasing the chrome to iron ratio of chromites products. More particularly, it relates to a chlorination method for increasing the chrome to iron ratio of chromites.

BACKGROUND OF THE INVENTION

In the geological environment, the primary industrial source of chromium is the mineral chromite, which can be represented by the ideal formula $FeO.Cr_2O_3$. In practice, FeO can be substituted by other elements such as MgO, CaO, MnO and Cr_2O_3 by Fe_2O_3 and Al_2O_3. These substitutions are at the origin of different types of chromites distinguished, among other things, by their chrome to iron ratios. In the geological environment, the chrome to iron ratios of chromites varies from 1.3 to 4.0 in many stratiform or podiform deposits. Chromites showing higher than 3, chrome to iron ratios, are rare in nature.

The principal utilization of chromites is in the production of ferro-alloys. Chromites are employed in the production of ferrochrome, a master alloy in the stainless steel industry. The primary process for the production of ferrochromium is described by the general reaction: metal oxide + reductant + energy $\Rightarrow$ (ferro)metal + reductant oxide. The production of ferrochromium is an energy-intensive process and is generally conducted in an electrical furnace. Ferrochromiums can be divided in three classes based on their carbon content: high carbon ferrochromium containing between 4 to 10 % carbon; medium carbon ferrochromium containing between 0.5 to 4 % carbon; low carbon ferrochromium containing less than 0.5 % carbon. The chrome to iron ratio of the chromite ore

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used as a feed to the furnace, controls the chromium content of the ferrochromium. The value of the ferrochromium is mainly based on its chromium and carbon contents. The highest prices are obtained for ferrochromium showing high concentration in chromium and low carbon content. Similarly, the chromites economic values are set by their chrome to iron ratios: a chromite with a Cr/Fe ratio of 1.5 being worth less than a chromite with a Cr/Fe ratio of 4. The economic value of these chromium-enriched chromites is increased in their use as enriched product directly and as feed for ferrochromium production.
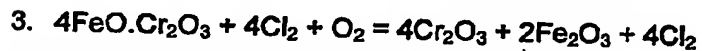
Hence, there is a need for a method for increasing the chrome to iron ratio of a chromite ore. Methods for achieving this goal have been described.

European Patent No. 0 096 241, by Robinson and Crosby, describes the chlorination of chromites mixed with coke by Cl_2 at a temperature ranging between 1000° and 1100° C. The chromites are completely transformed into chlorides and volatilized. The iron chlorides and chromium chlorides are separated according to their respective boiling points. This specific process leads to the formation of pure $CrCl_3$.

South African Patent No. 96/4584 by Lalancette, Bergeron, Bossé, Clerk teaches the chlorination of chromites by Cl_2 in the presence of air, no reductant being used. The process is described by two reactions.

1. $2FeO.Cr_2O_3 + 3Cl_2 = 2FeCl_3(g) + 2Cr_2O_3 + O_2$

2. $2FeCl_3 + 3/2O_2 = Fe_2O_3 + 3Cl_2$
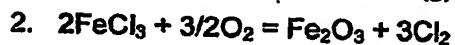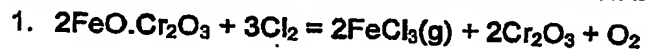
The combination of these two reactions results in:

3. $4FeO.Cr_2O_3 + 4Cl_2 + O_2 = 4Cr_2O_3 + 2Fe_2O_3 + 4Cl_2$

According to this process, the iron is selectively chlorinated and transformed in gaseous $FeCl_3$. While $FeCl_3$ is still in the reaction vessel, this product is rapidly transformed in Fe_2O_3 via reaction No. 2. This result in the production of a chromite showing an increase in its chrome to iron ratio with a simultaneous formation and precipitation of Fe_2O_3 as hematite in the chlorination reactor. After the chlorination

step, the reactor is drained and the hematite is dissolved in concentrated HCl leaving a residue of enrich chromite.

U.K. Patent No. 1,567,841 by Sowden and Rigg teaches the chlorination of $Cr_2O_3.xH_2O$ by CCl_4 below 600 ^0C. The resulting product is $CrCl_3$. The reaction at the base of this process is:

2 $Cr_2O_3.5/2H_2O$(amorphous) + 11/2 CCl_4 = $4CrCl_3$ + 11/2 CO_2(g) + 10 HCl(g). Following the chlorination reaction $CrCl_3$ is dissolved in diluted HCl.

Thermodynamic and kinetic studies of the chlorination of chromites and associated oxides such as FeO, Fe_2O_3, and Cr_2O_3 have also been published by Martirosyan (1978 a, b; Arm. Khim. Zh. 31, pp. 93-99; 100-106); and Kanari, Gaballah, and Alain (1998, Metallurgical and Materials Transactions B, 30B, pp. 577-587) for instance. These studies were centered on thermodynamic and kinetic considerations and do not teach how to apply these principles to a workable and optimized method.

Chlorination as a general metallurgical approach has also been described. Johnstone, Weingartner and Winsche (1942, J. Am. Chem. Soc., 64, pp. 241-244) observed the formation of a eutectic point when studying the binary system ferric chloride-sodium chloride. Cook, and Dunn (1961, J. Phys. Chem., 65, pp. 1505-1511) refined the phase diagram and presented evidence for the formation of $NaCl.FeCl_3$. Bezukladnikov, Tarat and Baibakov (1974, Zr. Prikl. Khim. 47, pp. 1722-1725); and Zhao, Tian and Duan (1990, Metallurgical Transactions B, 21B, 131-133) studied the solubility of chlorine in different molten salts. These authors concluded that the presence of $FeCl_2$ in molten salts increases by two orders of magnitude the speed of the chlorination reactions. They attributed this increase to the catalyst role played by $FeCl_2$ according to the reaction: $FeCl_2$(melt) + $0.5Cl_2$(gas) = $FeCl_3$(melt). The actual partial pressure of chlorine at the reaction site decreases rapidly causing decomposition of $FeCl_3$ with the liberation of chlorine at the reaction sites. $FeCl_2$ reacted with external chlorine

thus regenerating $FeCl_3$. This system increases chlorine diffusion and acts as a transport procedure for chlorine at the reaction sites and accelerates the chlorination process.

It is apparent from the foregoing that known methods are limited to the production of $CrCl_3$ at very high temperature (i.e. 1000°C), or to the formation of secondary hematite (Fe_2O_3) that has to be leached by concentrated HCl in order to produce chromites showing high chrome to iron ratios, and that known thermodynamic and kinetic studies on chlorination of chromites have not incorporated the effect of the catalyst role played by $FeCl_2$, $FeCl_3$ in the presence of molten salts and they do not integrate the required systems for the set up of a commercial process such as those taking account environmental requirements. Furthermore, these studies do not teach how to avoid potential problems related to the consumption of chlorine by others oxidic constituents occurring in the natural spinels structure of chromites and in other silicated phases associated with the ore

As an example of this last point, investigations on the chemical compositions of chromites from the Menarik Complex, Bay James, Québec, Canada, have showed that the oxidic components of the chromite ores are highly variable. Table 1 shows chemical analysis performed by an electron micro-probe of chromite grains extracted from Cr-3 chromite showing of the Menarik Complex. These results indicate important variations in the major oxides phases on a grain-to-grain basis. The average chemical composition of the Cr-3 mineralized zone is reported in the Table 2 with the heading Starting ore.

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Table 1. Chemical analysis of chromite grains by electron micro-probe, Menarik
Cr-3 chromite showing.

Sample No.	MgO %	Al$_2$O$_3$ %	SiO$_2$ %	TiO$_2$ %	V$_2$O$_3$ %	Cr$_2$O$_3$ %	MnO %	FeO %	Cr/Fe N/A
Cr3-26	7.74	17.23	0.00	1.28	0.58	45.59	1.23	26.36	1.52
Cr3-27	3.98	17.59	0.00	0.50	0.35	41.81	1.82	33.95	1.08
Cr3-37	2.93	16.45	0.00	0.00	0.36	44.87	1.19	34.19	1.16
Cr3-35	2.58	17.41	0.79	1.02	0.95	40.81	1.97	32.14	1.12
Cr3-29	1.83	15.67	0.00	0.00	0.87	42.77	1.72	36.01	1.05
Cr3-28	1.75	3.10	0.98	0.00	0.00	44.72	1.27	48.17	0.82
Cr3-44	2.73	5.92	0.82	0.72	0.79	42.10	0.93	46.00	0.81
Cr3-43	1.48	5.23	0.49	0.00	1.25	41.06	2.68	47.81	0.76

N/A: not applicable.

There thus remains a need to develop an effective method for the selective extraction of iron from heterogeneous natural chromites in such a way that other oxides such as CaO, MgO, MnO, SiO$_2$, TiO$_2$, Cr$_2$O$_3$ are substantially left unaffected by the method in such a way that the method remains secure. There also remains a need for a method able to extract the iron without the need to dissolve the hematite coatings on chromite with concentrate HCl, a complicated and expensive procedure. There also remains a need for a method including a catalyst component to accelerate the chlorination process and efficient environmental and recycling systems.

It is an object of the present invention to alleviate the drawbacks of the prior art.

Other objects and further scope of applicability of the present invention will become apparent from the detailed description given hereinafter. It should be understood, however, that this detailed description, while indicating preferred embodiments of the invention, is given by way of illustration only, since

various changes and modifications within the scope of the invention will become apparent to those skilled in the art.

SUMMARY OF THE INVENTION

According to a particular embodiment, the present invention comprises procedures allowing secure disposal of the iron extracted from the chromites.

According to a further embodiment, the present invention comprises procedures allowing recycling of the principal chemical reactants employed in the process.

According to a further embodiment, the present invention comprises means to minimize the production of Cr+6, a know carcinogen contaminant. In a specific embodiments, the means include using a reducing atmosphere during the gas solid interactions.

The present invention is applicable to chromite ores and different types of concentrates including alluvial chromites. If concentrates are used as feed to the invention, the concentrates can be obtained, after grinding of the ore, by the use of standard mineral processing technologies such as jigs, spirals, flotation units, and multi-gravity separator. The parameters related to the production of the chromite concentrates are outside the scope of the present invention. In general, the present invention provides a novel approach for the extraction of iron from chromites without substantially affecting other major chemical components.

According to a first embodiment of the present invention, there is provided a method for increasing the chrome to iron ratio of chromite product comprising iron oxide selected from the group consisting of ore and ore concentrate comprising the steps of contacting a mixture of the chromite product

with a mixture of salts of different compositions such as NaCl with chlorine and carbon monoxide in a reactor maintained at a temperature between about 250° and about 750° C whereby a portion of iron oxide in converted into gaseous iron chloride.

According to another embodiment of the present invention, there is also provided a method for increasing the chrome to iron ratio of chromite product comprising iron oxide selected from the group consisting of ore and ore concentrate comprising the steps of: obtaining chromite product having a grain size suitable to enable sufficient contact between the chromite product and the reacting gases, in a specific embodiment, the grain-size is between about 125 μm to about 300 μm, to yield a homogeneous grain-size chromite product; obtaining a mixture of salts of different compositions such as NaCl, and chromite product, wherein this mixture acting as a catalyst for the chlorination reactions and wherein the concentration of NaCl is between about 5 % and about 15% (w/w); drying the mixture wherein in a specific embodiment the temperature is of about 180 °C and the duration of the drying is of about 30 minutes to about 2 hours to yield a dry mixture; reacting the dried mixture with a gaseous combination of Cl_2 and CO at a temperature between about range 250° and about 750° C in a reactor so as to produce $FeCl_3$ by the reaction $FeO.Cr_2O_3 + 1.5Cl_2(g) + CO(g) \Rightarrow Cr_2O_3 + FeCl_3(g) + CO_2(g)$, whereby gaseous Cl_2 may exit the reactor; condensing the $FeCl_3$ to yield a $FeCl_3$ condensate. In a more specific embodiment, the method further comprises any of the steps of washing the $FeCl_3$ condensate with an aqueous solution to yield an aqueous solution rich in $FeCl_3$; reacting gaseous Cl_2 with metallic iron to yield an aqueous solution of $FeCl_3$; burning CO with air to yield gaseous CO_2; neutralizing the aqueous solution rich in $FeCl_3$ with NaOH by the reaction $FeCl_3(aq) + 3NaOH(aq) \Rightarrow Fe(OH)_3(s) + 3NaCl(aq)$ to yield an aqueous solution containing NaCl and an iron hydroxides precipitate; separating the aqueous NaCl solution from the iron hydroxides precipitate to yield a clearer aqueous NaCl solution and a iron hydroxides cake filter, the iron oxide cake being disposable in a regulated tailing pound; electrolyzing the NaCl solution to yield Cl_2, NaOH and H_2;

recycling at least one of Cl_2 andr NaOH as reactants for the chlorination and neutralization reactions; recycling H_2 as additional combustible for the chlorination furnace;and recovering the solid material from which the iron has been extracted by the chlorination reaction. In a specific embodiment, the chlorination is performed in a furnace built with material resistant to chlorine, to yield a $FeCl_3$ gaseous stream and a solid material from which the iron has been extracted and whereby residual chlorine may exit the furnace.

IN THE DRAWING

Figure 1 illustrates a flow diagram according to a specific embodiment of the present invention;

Figure 2 graphically illustrates a phase diagram of a system $FeCl_3$- NaCl, adapted from Cook and Dunn (1961);

Figure 3 graphically illustrates the carbochlorination of chromites, ΔGoT versus T;

Figure 4 graphically illustrates variations of the chrome to iron ratios with T° C during preliminary experiments;

Figure 5 graphically illustrates variations of chrome to iron ratios with time. The temperature used was 600° C and the NaCl concentration was 4.8 % (w/w); and

Figure 6 graphically illustrates variations of the chrome to iron ratios with reaction time. Triangle: T = 550o C ; square: T = 600o C ; circle: T = 673o C.

DESCRIPTION OF THE PREFERRED EMBODIMENT

Referring to Figure 1, the feed used can be ore or an ore concentrate obtained from an appropriate mineral processing technology. For the examples presented below, the experiments were performed on a massive chromite layer obtained from the Menarik deposit (James Bay, Quebec). The

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average mineralogy of 29 massive chromite layers of the Menarik Complex is: chromite 45 %, chlorite 32 %, serpentine 13 %, magnetite 3 %, talc 1 %, hornblende 4 %, and traces of sulfides. The sample was hand picked from the chromite mineralized zone Cr-3 and subsequently grinded to 125 µm. The chemical composition of this starting material, identified as the feed on Figure 1, is reported at the Table 2 as starting ore for the examples 1 and 2 , given thereafter, and at Table 3 as starting ore for the examples 3 to 6.

MIXING

NaCl was added to the grinded ore as a solution in order to obtain a 5 % concentration (w/w) of salt in the feed. The NaCl salt addition provides one of the components for the formation of an eutectic point which the $FeCl_3$ produces via the carbochlorination of the chromite feed (reactions are reported under the carbochlorination heading below). The phase diagram for the system $FeCl_3$-NaCl is illustrated at Figure 2.

For temperatures over the first eutectic temperature, 157° C, liquid $NaFeCl_4$ is formed from the reaction of $FeCl_3$ with NaCl. In the examples presented below, the chlorination temperature varies from 250° to 673° C. According to the phase diagram of Figure 2, $NaFeCl_4$ is present as a liquid phase in the feed at all chlorination temperatures used. Although the exact mechanism of action of the salt addition is not clearly known, previous works pointed towards the effect of catalyst of different salts addition on chlorination reactions in general. In the present invention, the salt addition is performed in order to produce a thin film of a melt around each grain of the feed. This interstitial melt contains the chlorination agent, under a chemical form such as $NaFeCl_4$. The thin film acts as a chlorination solvent increasing chlorine diffusion in the chromite. The chlorine gaseous atmosphere enclosed in the reactor regenerates the effective chlorination agent contained in the melt. It is understood that other types of salts such as KCl can be used to produce a catalytic system for the carbochlorination of chromites, this being obvious from the description of the present invention.

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DRYING AND PRE-HEATING

The drying step ensures a complete removal of water resulting from the salt addition and can be carried out at different temperatures and time periods. In the examples presented below, the charge was dried at 180 °C for 30 minutes. After cooling, the charge was transferred in the chlorination reactor and pre-heated at the selected reaction temperature.

CARBOCHLORINATION

The chemical reaction used in this step is the following:

4. $FeO.Cr_2O_3 + 1.5Cl_2(g) + CO(g) \Rightarrow Cr_2O_3 + FeCl_3(g) + CO_2(g)$

The $\Delta G°_T$ versus temperature of this reaction was calculated using the HSC software of Outokumpu. They are presented at Figure 3. For the span of temperatures considered,The $\Delta G°_T$ values are, inferior to $-$ 150 Kjoules. This demonstrates the thermodynamic feasibility of the reaction. According to reaction 4, the iron contained in the chromite reacts with Cl_2 to form $FeCl_3$. At the temperature range described in the examples presented below, 250° to 673° C, $FeCl_3$ is in a vapor state. Because of the continuous flow of gas passing through the reactor, $FeCl_3$ is carried outside the reactor, where it is condensed. An acceptor for the oxygen liberated during the chlorination reaction such as CO(g) may be added to maintain reducing conditions. as. The addition of CO(g) impede the reaction $2FeCl_3 + 3/2O_2 = Fe_2O_3 + 3Cl_2$ to occur. Therefore, no precipitation of unwanted solid hematite takes place in the reactor.

Another reaction of interest is the formation of ferrous chloride $FeCl_2$ during the carbochlorination phase. A rapid chlorination of $FeCl_2$ into ferric chloride $FeCl_3$ according to the reaction $2FeCl_2 + Cl_2 \Rightarrow 2FeCl_3(g)$is desirable, $FeCl_2$ having a high melting point of 670° C may be desirable according to specific embodiments in order to avoid the production of a diffusion barrier by the formed ferrous chloride , which may decreases the chlorine access to the reaction sites.

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Rhee and Shon (1990, Metallurgical Transactions B, 21B, pp. 321-330) reported data on the carbochlorination of ilmenite (FeO.TiO$_2$), a product presenting similarities to chromites when chlorinated. They showed that the kinetics follow a pore-blocking rate law . Zhao, Tian and Duan (1990, Metallurgical Transactions B, 21B, 131-133) studied the equilibrium between ferrous and ferric chloride in molten chloride salts. They concluded on the catalytic effect of the combination of salt and iron chloride and also on the volatilization of iron from the salt melt. Their data indicated that volatilization of iron as FeCl$_3$ is maximized when NaCl content, in a given melt, is high. Hence, in the present invention carbochlorination experiments were realized with NaCl to produce a catalytic melt when NaCl combines with FeCl$_2$ and/or FeCl$_3$ and to increase the volatilization (the removal) of iron as gaseous FeCl$_3$ from the carbochlorination reactor. None of these conditions were tested before on chromites.

When the chlorination temperature was reached, a mixture of Cl$_2$ and CO and N$_2$ was introduced in the reactor. After a few minutes, the FeCl$_3$(g) was expelled from the reactor. According to specific embodiments described in the examples below, the temperature was varied from 250° to 750° C. In specific embodiments, chlorine and carbon monoxide were used only on a 1/1 basis. The flow rate was maintained to 1 ml per second. For the subsequent experiments, a mixture of Cl$_2$, CO, and N$_2$ was employed, N$_2$ acting as a carrier gas. In these cases, the flow rates of the different gases were varied, as well as the weight % of salt additives.

The chlorination reactions were conducted in a simple horizontal static furnace. Usually, at industrial scale, chlorination is realized in fluidized bed reactors constructed of acid resistant bricks enclosed in a metal shell. In fluidized bed reactors, thesalt addition results in the formation of a thin liquid film layer around the chromite grains, which increases their adherence properties. For the purpose of the examples presented below therefore, it was decided to avoid fluidized reactor and the problems associated with grains agglomeration and bed sedimentation. Alternatives to fluidized bed reactor include a vertical static reactor

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and a horizontal rotating reactor. Other possible arrangements include the addition of solid reducing agents like coal, coke in replacement of CO. Pelletizing-sintering procedures, similar to the ones employed in the ferrochromium industry, can be performed before the chlorination step.

After the chlorination reaction, the solid minerals contained in the reactor were dumped. Depending on the duration of the reaction, the gas flow rate, the salt additives, the Cl_2/CO mixture, the chlorinated solid residue showed an increase in its chrome to iron ratios. The ratios varied from 1.5 in the starting ore before chlorination up to 10 after chlorination. These results are presented in Tables 2, 3 and 4 below.

CONDENSER

Gaseous $FeCl_3$ exits continuously the reactor during the reaction and the abrupt temperature drop outside the reactor, causes its fast condensation in the top section of the condenser. The condenser is placed at an adequate distance from the furnace so as to keep its temperature below 50 ^oC. $FeCl_3$ is highly soluble in water. A small volume of water is added to the condenser apparatus to wash the solid $FeCl_3$. The $FeCl_3$ rich aqueous solution accumulates at the base of the condenser and is directed into a reservoir for subsequent neutralization. The other gases leaving the reactor are essentially Cl_2, CO, CO_2 and N_2. These gases are apparently not affected by the presence of the condenser and flow through it without experiencing any detectable change in their compositions or states and exit the condenser.

WASHING TOWER AND GAS TREATMENT

Cl_2, CO, CO_2 and N_2 exiting the chlorination reactor are routed toward a washing tower. Scraps of metallic iron in the millimeter range are placed in the tower and sprayed with a small quantity of water in order to keep wet the iron metallic surfaces. This arrangement favors the reaction $Fe(s) + 3/2Cl_2 \Rightarrow$

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FeCl₃(aq) which consume the unreacted Cl₂. After the reaction, FeCl₃ is present as a solute in H₂O. CO and CO₂ percolate up and exit the washing tower near the top. CO is burned as CO₂ in an after burner unit. If necessary, by environmental regulations, the scrubbing of CO₂ can be achieved by an existing complementary technology. The aqueous FeCl₃ solution flows out at the base of the washing tower to be routed toward the neutralization reservoir.

NEUTRALIZATION

The aqueous FeCl₃ solutions coming from the condenser and the washing tower are pumped in a neutralization reservoir. A solution of NaOH is added to the tank. The ferric chloride reacts with NaOH according to the reaction:

$$FeCl_3(aq) + 3NaOH(aq) \Rightarrow Fe(OH)_3(s) + 3NaCl(aq)$$

After completion of the reaction, the solid amorphous iron oxides are isolated from the liquid phase by an appropriate solid-liquid separation such as centrifugation or press filtration. The filtration cake is discharged to the tailings. The aqueous NaCl solution is directed to an electrolysis cell.

ELECTROLYSIS

The NaCl solution, obtained from the neutralization section of the process, is electrolyzed by a chlor-alkali membrane cell process. The reaction involved is:

$$2NaCl(aq) + 2H_2O \Rightarrow H_2(g) + Cl_2(g) + 2NaOH(aq)$$

The gaseous Cl₂ and aqueous NaOH generated by the reaction are recycled in the process. The Cl₂ is returned to the carbochlorination reactor and the aqueous NaOH in the neutralization section. The H₂(g) produced by this reaction can be employed as the main energy source or an additional energy source for the carbochlorination furnace. External supplies of NaCl can be used if needed.

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Any means for routing, transporting and transferring solid, gas, liquid and pulp are within the scope of these inventions. The present invention is described in further details by the following non-limiting examples.

EXAMPLES

The implementation and results of the examples provided herein are summarized in Tables 2, 3 and 4. Table 2 presents results according to the first set of embodiments of the present invention for which the Cl_2/CO ratio flow rates, type and quantity of salt addition were kept constant during the experiments, while the temperature was varied. Examples 1 and 2 are derived from this first set of embodiments. Tables 3 and 4 contain data for the second set of embodiments for which, temperature, reaction time and quantity of salt addition were varied. This second set of embodiments was used to establish examples 3 to 6.

The carbochlorination experiments where carried out in a 65 cm long horizontal cylindrical furnace equipped with a type K pyrometer linked to a thermostat controller. Usually, a 10 grams sample was placed in a ceramic beaker and inserted in a silica fused tube. The beaker-tube assembly was then introduced in the furnace.

The major and trace elements were analyzed by inductively couple plasma atomic emission spectroscopy, ICP-AES, after a fusion procedure specifically applicable to chromite. Sulfur was determined with a CNS analyzer.

Table 2. Results for thirst set of embodiment conducted with temperature changes only.

SAMPLE	GAS	T	Cr/Fe	SiO₂	Cr₂O₃	TiO₂	Al₂O₃	Fe₂O₃T	MnO	MgO	CaO	Na₂O	K₂O	P₂O₅	LOI	S	Total
		(°C)		%	%	%	%	%	%	%	%	%	%	%	%	%	%
Starting ore	NA	NA	1.76	4.72	45.33	0.35	13.26	25.31	1.01	12.11	0.15	0.21	<0.028	<0.021	0.35	0.06	103.2
Test-01	Cl-CO	250	1.87	4.00	47.11	0.37	13.12	24.69	0.96	10.82	0.20	0.26	<0.038	<0.019	0.44	0.07	102.4
Test-02	Cl-CO	350	2.15	3.96	49.29	0.38	13.48	22.46	0.82	10.43	0.20	0.26	<0.044	<0.022	1.59	0.08	103.3
Test-03	Cl-CO	450	2.27	3.36	51.56	0.39	13.17	22.21	0.71	10.65	0.25	0.32	<0.062	<0.031	1.06	0.09	104.1
Test-04	Cl-CO	550	2.98	2.33	52.07	0.37	14.15	17.12	0.81	12.73	0.11	0.14	<0.026	<0.013	0.69	0.04	100.9

$Cl_2/CO = 1$; 5 % NaCl (w/w) addition; LOI: lost on ignition; Fe_2O_3T: (T) stand for total iron

Table 3. Reaction conditions and results for the second set of embodiments.

SAMPLE	T	NaCl	Time	F(Cl₂)	F(CO)	F(N₂)	Weight loss	Fe₂O₃	Cr₂O₃	Cr/Fe
	°C	%	(h)	ml/min	ml/min	ml/min	%	%	%	
Starting ore	21	0	0	0	0	0	0	25.50	47.82	1.88
T-2-1	600	0	2	220	220	110	11.01	15.60	49.23	3.16
T-2-2	600	0.8	2	220	220	110	12.29			
T-2-3	600	4.8	2	220	220	110	17.75	13.80	50.11	3.63
T-2-4	600	10.3	2	220	220	110	17.84	12.20	46.43	3.81
T-2-5	600	15.0	2	220	220	110	19.06	9.66	43.64	4.52
T-2-6	600	4.8	1.5	220	220	110	16.69	14.30	50.29	3.52
T-2-7	600	4.8	1	220	220	110	14.11	15.40	50.37	3.27
T-2-8	600	4.8	0.5	220	220	110	12.08	16.60	49.81	3.00
T-2-9	673	4.8	2.0	220	220	110	33.96	5.24	52.83	10.08
T-2-10	673	4.8	1.0	220	220	110	27.58	8.73	52.44	6.00
T-2-11	673	4.8	0.75	220	220	110	24.50	10.10	52.58	5.21
T-2-12	673	4.8	0.5	220	220	110	18.79	13.6	51.66	3.80
T-2-13	673	4.8	0.5	0	0	0	0	24.50	46.18	1.88

F: flow rate

Table 4. Major elements analyses, for the second set of embodiments.

	SiO₂ %	Cr₂O₃ %	TiO₂ %	Al₂O₃ %	Fe₂O₃T %	MnO %	MgO %	CaO %	Na₂O %	K₂O %	P₂O₅ %	LOI %	S %	Total %
Starting ore	2.60	47.82	.352	13.0	25.5	1.05	11.1	.173	.0260	<0.042	<0.21	#N/A	<0.042	102.1
T-2-1	2.45	49.23	.358	15.0	15.6	.948	12.0	.190	<0.034	<0.069	<0.34	1.25	<0.069	97.5
T-2-3	2.69	50.11	.346	15.7	13.8	1.07	12.7	.116	.593	<0.06	<0.3	1.45	<0.06	99.0
T-2-4	2.41	46.43	.314	14.5	12.2	1.03	11.8	.0960	2.96	<0.069	<0.35	7.35	<0.069	99.5
T-2-5	2.94	43.64	.275	13.2	9.40	.994	11.2	<0.019	6.62	<0.063	<0.31	12.14	<0.063	101.0
T-2-6	3.67	50.29	.343	14.8	14.3	1.08	12.5	<0.017	.322	<0.057	<0.28	1.27	<0.057	99.0
T-2-7	3.02	50.37	.399	14.6	15.4	1.06	12.2	<0.016	.447	<0.054	<0.27	2.57	<0.054	100.5
T-2-8	3.44	49.81	.345	14.2	16.6	1.05	11.9	<0.017	.783	<0.058	<0.29	1.67	<0.058	100.2
T-2-9	3.53	52.83	.330	20.0	5.24	.453	16.1	<0.017	.0330	<0.057	<0.29	0.94	<0.057	99.7
T-2-10	3.48	52.44	.336	18.2	8.73	.812	14.8	.0220	.0410	<0.053	<0.27	0.88	<0.053	100.0
T-2-11	3.32	52.58	.339	17.5	10.1	.977	14.3	.0150	.0660	<0.049	<0.24	0.65	<0.049	100.1
T-2-12	3.46	51.66	.348	15.8	13.6	1.08	13.1	.0310	.161	<0.047	<0.23	0.54	<0.047	100.2
T-2-13	3.07	46.18	.347	13.0	24.5	1.01	10.7	.0220	.205	<0.057	<0.28	1.27	<0.057	101.3

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EXAMPLE 1

Selectivity of the carbochlorination for the removal of iron versus chromium

This example comprises a set of 4 experiments. The results are presented in Table 2. The aim of these experiments was to verify the selectivity of the iron removal by carbochlorination versus chromium. Although the other major elements were analyzed, they are reported at Table 2 for indicative purposes only. The span of temperature studied varied from 250 to 550°C. The chlorinated sample were mixed with a NaCl brine and dried at 180°C for 30 minutes. The salt content of the chlorinated samples was 5 % (w/w). A 10 g sample of chromite ore was placed in a 10 ml porcelain beaker. The beaker was positioned in the center of 60 cm in length silica tube, with an internal diameter of 6 cm. The assembly beaker-silica tube was placed in the furnace and the temperature was raised at the chosen carbochlorination temperature. When the temperature was reached and sTable, a Cl_2, CO gas mixture was introduced in the furnace on a one to one ratio basis. The carbochlorination step was conducted for 60 minutes. Five minutes after the beginning of the gases introduction in the furnace, at the selected temperature, a red brown chlorine vapor formed. This vapor was expelled outside the reactor, by the gases flow, where it condensed on the inside wall of the silica tube. At the end of the experiment the furnace heating device and the gases flow were stopped. After a cooling period, the solid residue left in the porcelain beaker was analyzed for major and selected trace elements.

The results from Table 2 for Fe_2O_{3T} and Cr_2O_3 clearly show the removal of iron when compared to chromium for all of the four experiments. Hence the original content of iron decreases gradually with increase of the carbochlorination temperature from 25.31 % in the starting ore to 17.12 % in the Test-04 run at 550 °C. The chromium content of the samples tested slightly increases from 45.33 % starting ore to 52.07 % in the test-04 sample. This chrome enrichment was correlated with the weights losses of the samples and therefore reflected the removal of iron from the samples. As expected, the chrome to iron

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ratios show a positive correlation with the temperature (Figure 4). The chrome to iron ratio increases from 1.76 in the starting ore up to 2.98 in the Test-04 sample.

EXAMPLE 2
Identification of the condensate as FeCl₃

The red brown condensate formed on the inside wall of the silica tube (in experiment described in Example 1) was washed out from the tube with water, in which this compound dissolved readily. This solution was analyzed by ICP-AES for major elements and by UV spectroscopy for the oxidation state of iron. Analyzis of the solution established the presence of iron as the only major element. Other elements were present at the trace level. Iron oxidation state was determined as Fe^{+3} by UV. These observations further demonstrated that iron was removed as gaseous $FeCl_3$ during the carbochlorination of the chromite ore.

EXAMPLE 3
Effect of the salt addition on the selective removal of iron versus chromium

The effect of the NaCl salt addition on the carbochlorination was tested by adding incremental quantity of NaCl to samples T-2-1 to T-2-5. The experimental conditions for these five samples are summarized in Table 3. Carbochlorination temperature was set to 600° C, the reaction time to 2 hours, the quantity of NaCl salt addition varied from 0 to 15.0 % (w/w). Results presented in Table 3 show a direct increase in the chrome to iron ratio in relation with the quantity of salt added to the feed. In the sample T-2-1, with no salt addition, the chrome to iron ratio reaches a value of 3.16 after the chlorination step, an increase of 1.75 compared to the original ore. In the sample T-2-5, to which was added 15 % NaCl (w/w), the chrome to iron ratio is 4.64 at the end of the chlorination experiment. This corresponds to a 47 % increase in the Cr/Fe when compared to sample T-2-1. This strong augmentation of the carbochlorination efficiency is attributed to the catalyst effect of the mixture NaCl and $FeCl_3$ as explained before.

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EXAMPLE 4

Effect of increasing the reaction time on the selective removal of iron versus chromium

The effect of increasing the reaction time on the selective removal of iron was tested by 0.5 hour time increments. Total reaction time varied from 0.5 hour to 2.0 hours. Samples employed for this test were, for a total reaction time of, 0.5 hour T-2-8, 1.0 hour T-2-7, 1.5 hours T-2-6 and 2.0 hours T-2-3. Experimental conditions used for these samples are reported at Table 3. The chrome to iron ratios increase from 1.8, for the starting ore, to 3.63 after a reaction time of 2 hours. The chrome to iron ratios augmentation is positively correlated to the reaction time (Figure 5).

EXAMPLE 5

Effect on increasing the temperature on the selective removal of iron versus chromium

Four carbochlorination experiments were carried out at 673 °C to investigate the effect of a temperature increase on the selective removal of iron versus chromium. These four experiments were conducted at different reaction times length. The reaction times length are similar to those of example 4. The samples employed were T-2-9 to T-2-12. The experimental conditions and the results are reported at Table 3. The temperature setting at 673 °C was pre chosen as slightly superior to the melting point of $FeCl_2$ (670° C). It was postulated that $FeCl_2$ is formed at some point during the chlorination and subsequently transformed in $FeCl_3$ according to the reaction $FeCl_2 + 1/2Cl_2 \Rightarrow FeCl_3(g)$. At temperature below the melting point of $FeCl_2$, the presence of this compound as a solid can act as a blocking agent between the chlorination agent and the chromites reaction sites. When melted $FeCl_2$ can actively play in the chlorination catalytic system already described in these inventions. The results indicated that rising the

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chlorination temperature to 673° C has a very decisive impact on the selective removal of iron versus chromium, with production of a chrome to iron ratio up to 10 for a two hours chlorination time. The relation between the chrome to iron ratio versus chlorination time is presented at the Figure 6.

A comparison between previous results for T = 550° C and T = 600° C and results at 673° C is presented at the Figure 6. In all cases the experiments run at 673° C showed important increases in the chrome to iron ratios when compared to the experiments run at lower temperatures. Moreover, the chrome to iron ratios between the experiments run at 550° C and 600° C show a relatively small increase, from 2.98 to 3.27 if compared to one obtained for the experiment run at 673° C, (6.00). It is proposed that the important increases in the chrome to iron ratios for the experiments run at 673° C are attributed to the melting of $FeCl_2$ and volatilization of $FeCl_3$. This melting allowed $FeCl_2$ to play a role in the catalytic system comprising NaCl, $FeCl_2$ and $FeCl_3$.

EXAMPLE 6

Effect of the carbochlorination for selectively removes iron without altering the major chemical components of the chromite

In the second set of experiments the major elements composition and the weight losses were measured and presented at Tables 3 and 4. When correcting for the weight losses due to the losses of iron (weight losses, Table 3), no apparent removal of other major elements was noticed by comparison to the starting composition. The Cr_2O_3 contents of samples T-2-4 and T-2-5 show small losses. They are attributed to a dilution effect by NaCl related to the large salt addition in these two samples, respectively 10 and 15 %. MnO and CaO showed slight decreases in their concentrations. These two components are present generally at concentrations lower than 1 % in chromites and their partial removal is not detrimental to the present invention.

Although the invention has been described above with respect to a few representative examples and drawings, it will be evident in the person skilled in the art that it may be modified and refined in various ways. It is therefore wished to have it understood that the present invention should not be limited in scope, except by the terms of the following claims:

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WHAT IS CLAIMED IS:

1.   A method for increasing the chrome to iron ratio of chromite product selected from the group consisting of ore and ore concentrate comprising the steps of contacting a mixture of the chromite product, a salt, chlorine and carbon monoxide in a reactor maintained at a temperature between about 250° and about 750° C whereby a portion of iron oxide in converted into gaseous iron chloride.
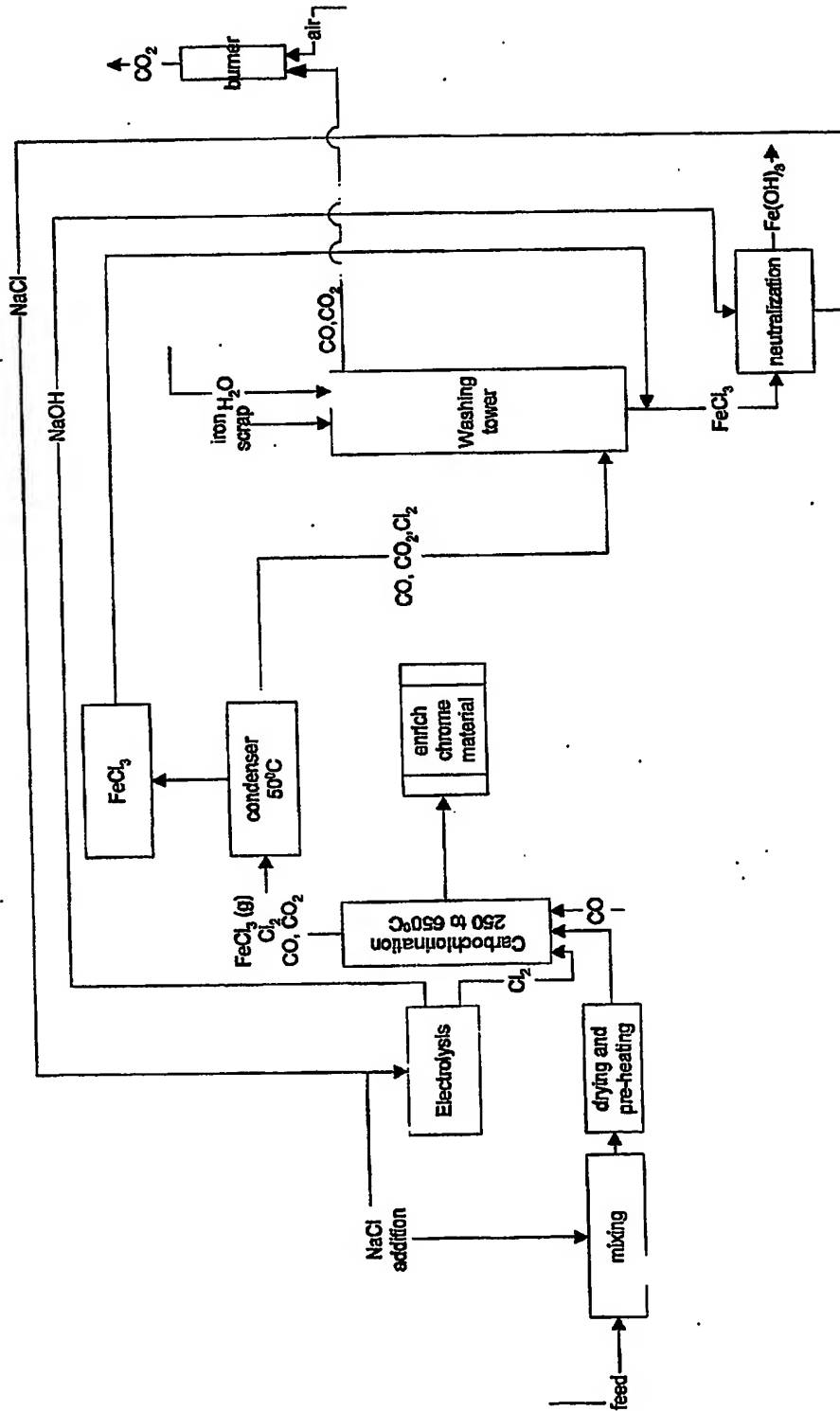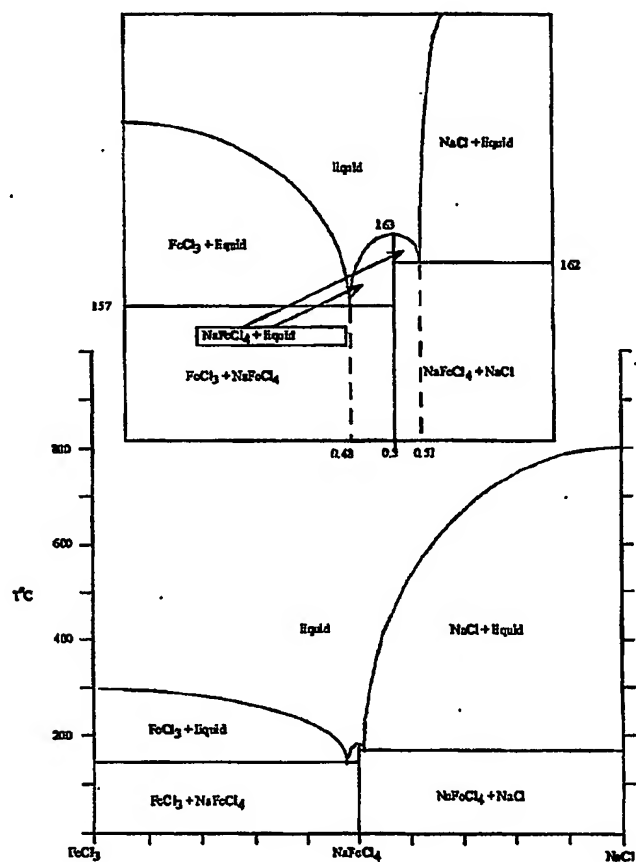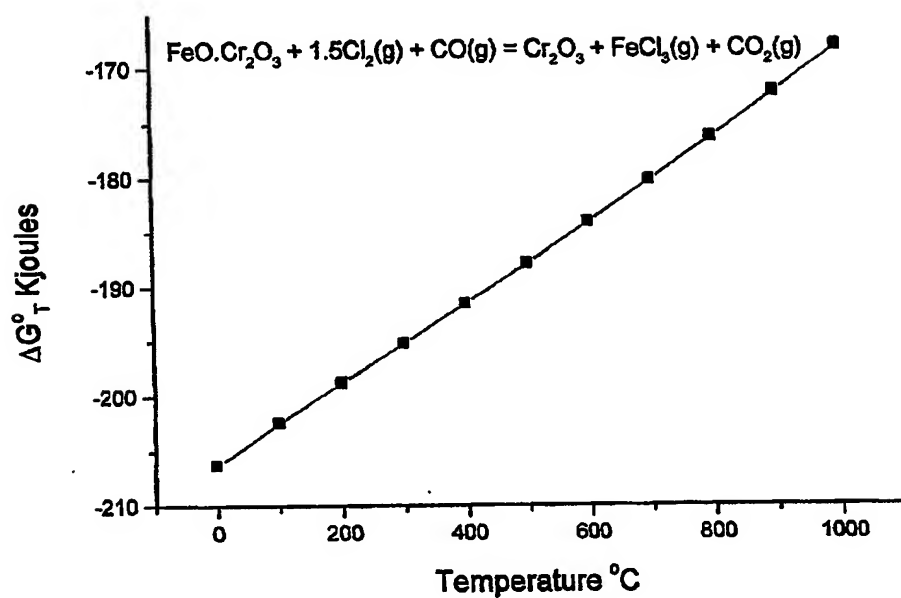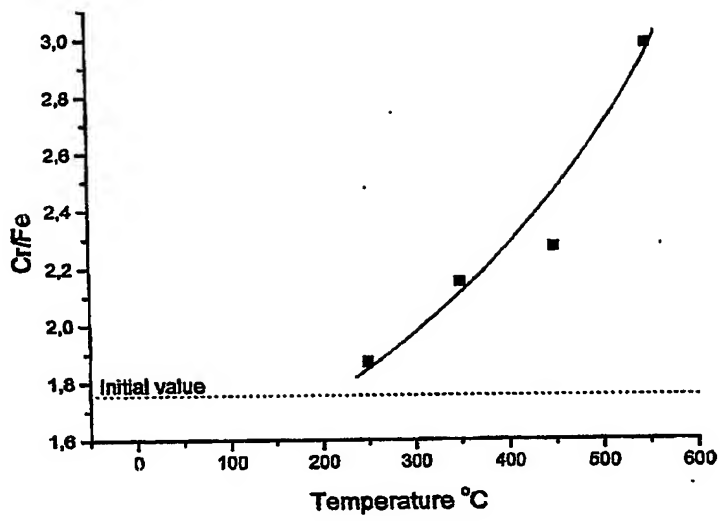
Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

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Figure 6